

Polymer Morphology

and

Polymer Transitions

Rosen Chapters V and VIII

Handwritten text at the top of the page, possibly a title or header, which is mostly illegible due to fading and bleed-through.

Handwritten text in the middle of the page, appearing as a single line or short paragraph, also mostly illegible.

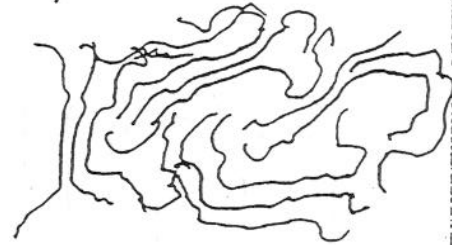
Handwritten text at the bottom of the page, possibly a signature or footer, which is mostly illegible.

Polymer Morphology (Rosen, ch. V)

Amorphous vs Crystalline (semi-)

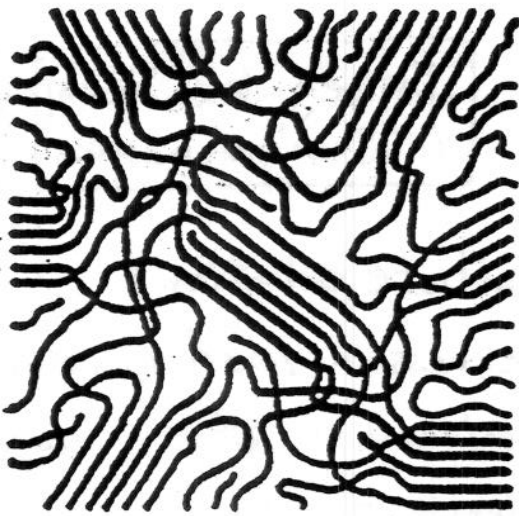


entangled, random coil

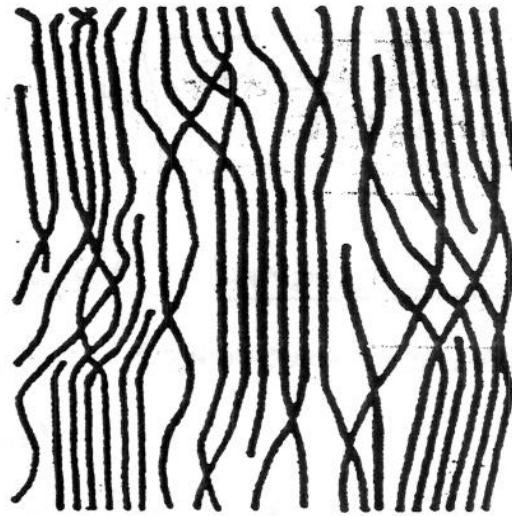


entangled, Aligned regions

Fringed Micelle Model.



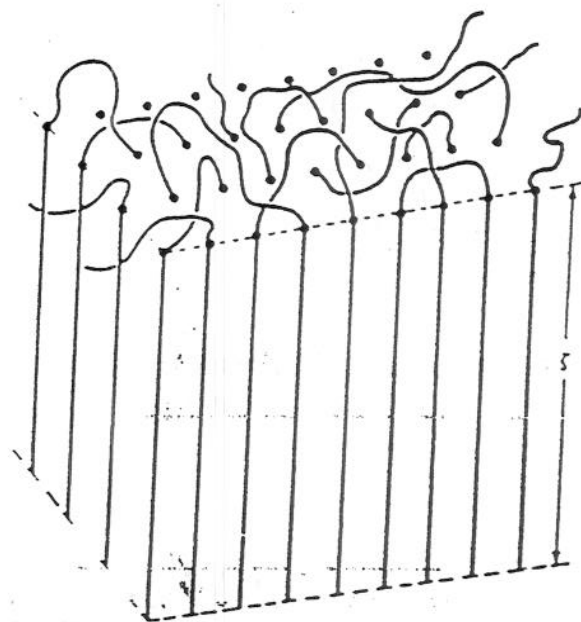
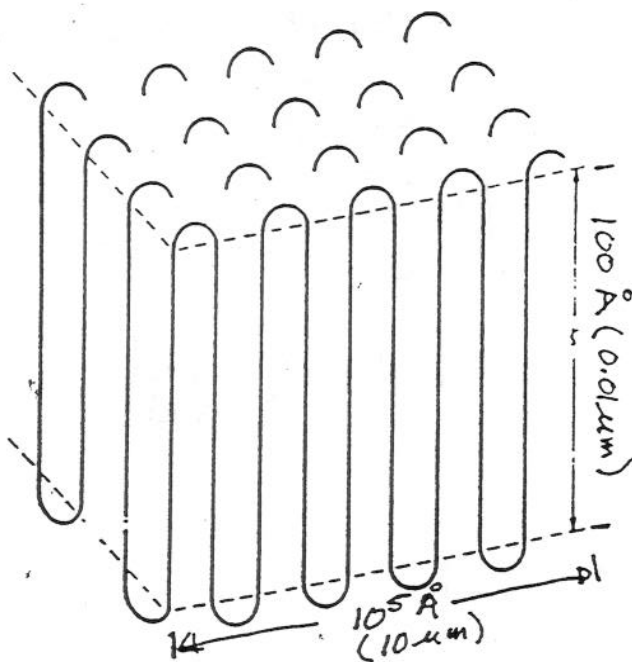
UNORIENTED



ORIENTED
(Stress field)

- "ORDERED DOMAINS" connected by "Amorphous" regions
- origin of the SEMI-CRYSTALLINE nature
- typical (high) crystallinity $\approx 85\%$
- effect of crystallinity on MECHANICAL Properties similar to cross-linking (but can be melted)

Lamellar Crystals (Chain Folded Model)



Adjacent Reentry
MODEL

Irregular Reentry
("Switchboard")

Single Crystal (from dilute solution)

- typical dimensions: thickness $\approx 100 \text{ \AA}$ ($0.01 \mu\text{m}$)
Length/Width $\approx 10^5 \text{ \AA}$ ($10 \mu\text{m}$)

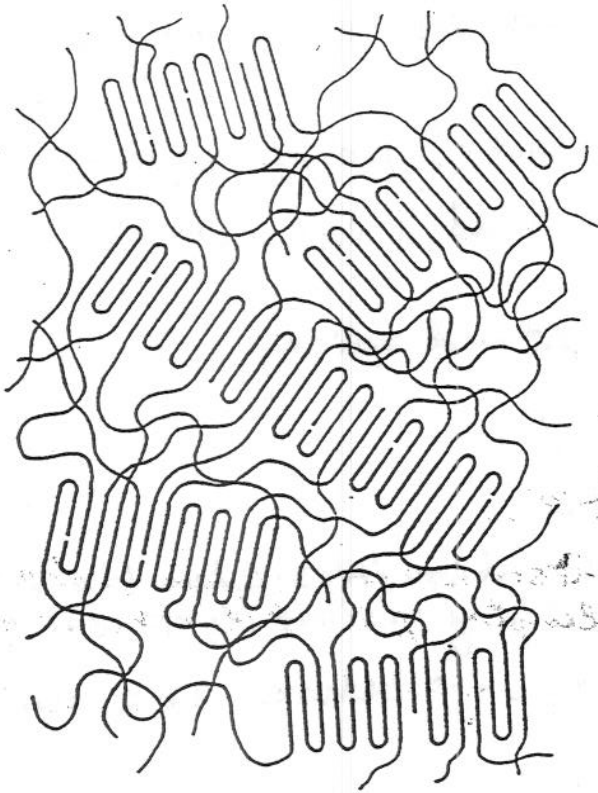
* Note: typical chain "extended" length $\approx 0.1 \mu\text{m}$.

Bulk (Melt) Crystallized.

- typical dimension: up to $1 \mu\text{m}$ (10^4 \AA) thick.
- MOST often "switchboard" Reentry

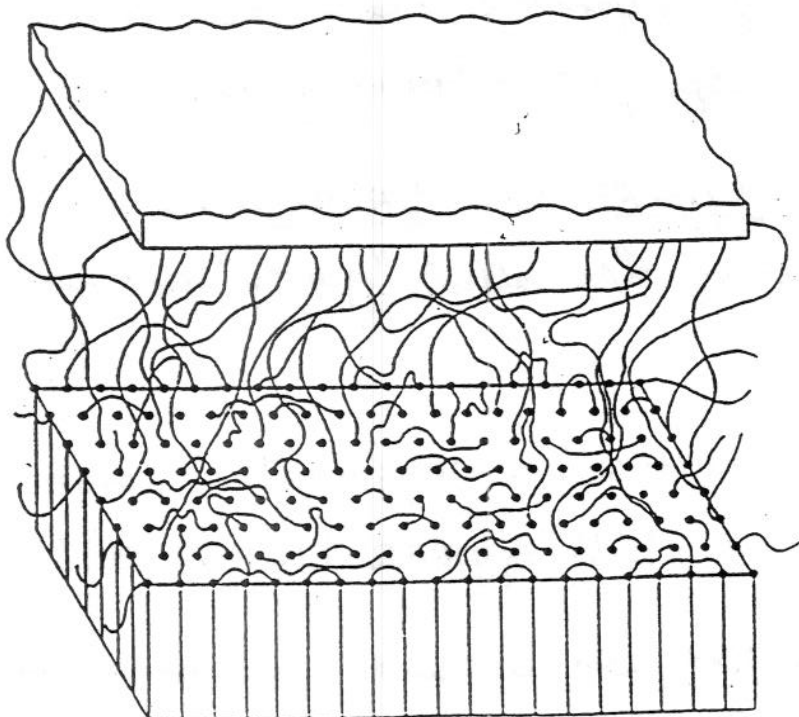
Chain-folded Lamella with Amorphous Tie
Molecules

Model for Melt Crystallized Polymers



2-D Perspective.

- Chain-folded (aligned) regions
- amorphous interlamellar Region
- very little adjacent reentry



3-D Perspective
(side view)

- "Switchboard"
REENTRY

① Mechanical Properties (Refer to Table S.1)

- increased strength and rigidity.
- greater ratio crystalline / Amorphous
 - stronger
 - more rigid
 - harder
 - less easily deformed.

E.g. Stereoregular (isotactic) polypropylene.

- crystallizable: hard, rigid plastic

Atactic PP

- Amorphous, soft and sticky.

② Optical Properties.

- light scattering at discontinuities when the size similar to wavelength of visible light (0.4-0.7 μ m).
ice → clear snow → white (air/crystal interface)
- semi-crystalline polymer → dense crystalline regions have higher refractive index than amorphous regions ∴ opaque or translucent
- AMORPHOUS POLYMERS are TRANSPARENT.
↳ that's why also called "glassy" polymers

Exceptions.

- very small crystallites in a crystalline polymer → the polymer can still appear transparent.
- copolymer or filler can be cause for translucent

Effect of Crystallinity on Mechanical Properties.

Table 5.1 The Influence of Crystallinity on Some of the Properties of Polyethylene*

Material product	Low density	Medium density	High density
Density range, g/cm ³	0.910-0.925	0.926-0.940	0.941-0.965
Approximate % crystallinity	42-53	54-63	64-80
Branching, equivalent CH ₃ groups/1000 carbon atoms	15-30	5-15	1-5
Crystalline melting point, °C	110-120	120-130	130-136
Hardness, Shore D	41-46	50-60	60-70
Tensile modulus, psi (N/m ²)	0.14-0.38 × 10 ⁵ (0.97-2.6 × 10 ⁸)	0.25-0.55 × 10 ⁵ (1.7-3.8 × 10 ⁸)	0.6-1.8 × 10 ⁵ (4.1-12.4 × 10 ⁸)
Tensile strength, psi (N/m ²)	600-2300 (0.41-1.6 × 10 ⁷)	1200-3500 (0.83-2.4 × 10 ⁷)	3100-5500 (2.1-3.8 × 10 ⁷)
Compressional modulus, psi (N/m ²)	0.08-0.6 × 10 ⁵ (0.34-4.1 × 10 ⁸)	0.6-1.15 × 10 ⁵ (4.1-7.9 × 10 ⁸)	1.0-2.6 × 10 ⁵ (6.9-18 × 10 ⁸)

* must be kept in mind that mechanical properties are influenced by factors other than the degree of crystallinity (molecular weight, tacticity, etc.).

Density : crystalline regions more DENSE than Amorphous

$$\frac{1}{\rho} = \frac{w_c}{\rho_c} + \frac{w_a}{\rho_a}$$

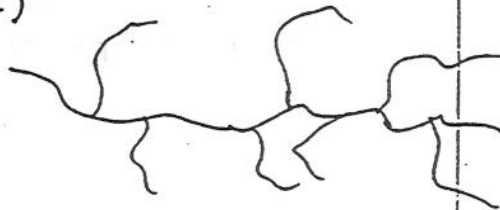
(c = crystalline
a = amorphous)

∴ density is a quick relative measure of crystallinity.

Polyethylene.

→ Low Density Polyethylene (LDPE)

- Long-chain branching



→ Linear Low Density PE (LLDPE): misnomer

- Short chain branching
- Medium density
- Copolymer (vinyl monomers)



→ High Density PE (HDPE)

- linear



EXAMPLES

- ① Polystyrene (Atactic) → transparent
• random phenyl group ARRANGEMENT
- ② Polystyrene (isotactic) → white
crystallizes
- ③ High Impact PS (dispersion of ~~the~~ polybutadiene rubber particles) → white

Problem.

- PE and PP produced by stereospecific catalysts
 - fairly rigid, translucent plastics.
- 65/35 copolymer blend → soft, transparent rubber

Why?

- PE linear → highly crystalline $\left[\text{C}-\text{C}-\text{C}-\text{C} \right]_n$
- PP isotactic → highly crystalline $\left[\text{C}-\underset{\text{CH}_3}{\text{C}}-\underset{\text{CH}_3}{\text{C}}-\text{C} \right]_n$
- 65/35 copolymer: Ethylene-Propylene Rubber (EPR)
 - Random copolymer $\left[\text{C}-\underset{\text{CH}_3}{\text{C}}-\underset{\text{CH}_3}{\text{C}}-\text{C}-\underset{\text{CH}_3}{\text{C}}-\text{C} \right]_n$
 - Amorphous, rubbery polymer.

ELASTOMERIC POLYPROPYLENE

Oscillating catalyst controls microstructure

Unprecedented control over the microstructure of polypropylene has been achieved by Stanford University chemists through use of an oscillating catalyst that, depending on its conformation, promotes two different types of propylene polymerization.

The catalyst produces polypropylene with a wide range of elastic properties, according to the polymerization conditions.

The catalyst is the first example of a new, inexpensive approach to producing block copolymers, says associate professor of chemistry Robert M. Waymouth, who carried out the research with graduate student Geoffrey W. Coates. Unlike traditional routes to block copolymers—in which a catalyst polymerizes different monomers sequentially—the new catalyst polymerizes a single monomer in two different ways [Science, 267, 222 (1995)].

Moreover, the product—elastomeric polypropylene—has real commercial potential, Waymouth notes. "Because elastomeric polypropylene is a thermoplastic, it is recyclable," he explains. "It is an elastomer only until it melts at a temperature higher than its use temperature."

In contrast, conventional thermoset plastics, whether natural or synthetic, derive their elasticity from covalent cross-linking of polymer chains. Because of these covalent bonds, rubbers cannot be recycled by melt processing.

Kenneth B. Wagener, a chemistry professor at the University of Florida, Gainesville, points out in a commentary in the same issue of Science (page 191) that polypropylene is the product of work in the 1950s by Karl Ziegler and Giulio Natta, who discovered a method for producing stereoregular polypropylene using a chiral catalyst. Ziegler and Natta shared the 1963 Nobel Prize in Chemistry for their work on polymers.

Today, polypropylene is one of the five largest volume plastics in use. Nevertheless, Wagener observes, the

work by Waymouth and Coates demonstrates that "even such a mature material as polypropylene can be the subject of dramatic advances in polymer chemistry."

Waymouth and Coates note that the stereochemistry of polyolefins, which can be described in terms of their "activity," strongly influences their properties. Isotactic polypropylene, in which all of the stereocenters of the polymer are the same, is a crystalline thermoplastic. By contrast, atactic polypropylene, in which the stereocenters are arranged randomly, is an amorphous gum elastomer.

Polypropylene consisting of blocks of atactic and isotactic stereosequences is rubbery. Although previous researchers have discovered catalysts that produce elastomeric polypropylene, "it has so far proven difficult to control the polymer structure and properties through a rational modification of the catalysts or reaction conditions," Waymouth says.

Waymouth and Coates built on the work of other researchers who showed that rigid, chiral metallocene catalysts produce isotactic polyolefins, whereas achiral forms of the catalysts produce atactic polyolefins. Their research was

supported by Amoco and the National Science Foundation.

The Stanford chemists prepared an unbridged metallocene catalyst with indenyl ligands that rotate about the metal-ligand bond axis. The rotation causes the catalyst to isomerize between chiral-like and achiral-like geometries.

When the catalyst is in the chiral-like geometry, it synthesizes a block of isotactic polypropylene; when it is in the achiral-like geometry, it generates a block of atactic propylene. As the ligands rotate, the catalyst produces alternating blocks of isotactic and atactic polymer, much like a miniature sewing machine switched back and forth between two different kinds of stitches.

One further trick is required to make the machine work. Indenyl ligands rotate so much faster than the polymerization reaction that stereoregular polymer blocks don't form. To overcome this, Waymouth and Coates add a phenyl substituent to the ligand to slow down the rate of rotation—so that it is slower than that of monomer insertion yet faster than the time required to construct a complete polymer chain. Thus, several monomers are incorporated into the growing polymer chain before the

switch is thrown to produce the next block type.

The specific compound Waymouth and Coates synthesize is bis(2-phenylindenyl) zirconium—which is abbreviated as (2-PhInd)₂ZrCl₂. They derived their catalyst from (2-PhInd)₂methylaluminoxane.

"One of the most remarkable powerful attributes of this catalyst system is the sensitivity of the polymer microstructure to the reaction conditions," Waymouth stresses. As monomer concentration is increased, the isotacticity of polypropylene also increases—behavior that is consistent with the polymerization mechanism the catalyst was designed to follow.

The microstructure of polypropylene is commonly described in terms of "isotactic pentad content," which is a fraction of stereosequences containing five adjacent isotactic stereocenters. Varying reaction conditions, Waymouth says, the new catalyst produces polypropylenes with isotactic pentads ranging from 6.3 to 28.1%.

"Other researchers have made very stiff polypropylene," he adds. "Because we are beginning to understand how our catalyst works, we can control the properties of the polypropylene in a huge range. We can produce material that can be stretched to eight times length and snaps back, or we can produce material that is very stiff and hard."

Kathy E.

* Structure Property Relationship Slap

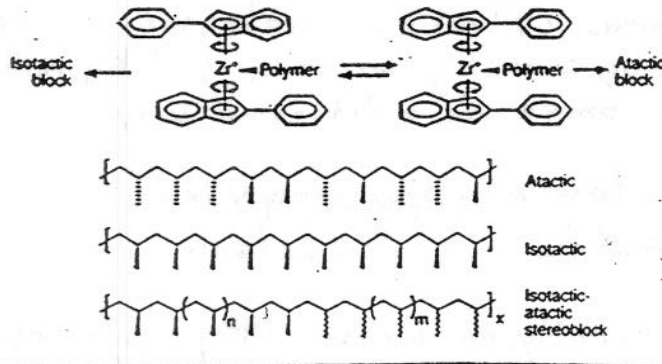
Altered bacteria make ethanol from xylose

Researchers have achieved significant efforts to develop genetically engineered bacteria that can produce ethanol efficiently from plant biomass for use as alternative transportation fuels.

Scientists at the Department of Energy's National Renewable Energy Laboratory (NREL) in Golden, Colo., genetically modified the bacterium *monococcus mobilis*—whose natural product produces ethanol from the six-carbon (hexose) sugars glucose and fructose—and the disaccharide sucrose—so that it also makes ethanol from the five-carbon (pentose) sugar xylose.

Glucose and xylose are major breakdown products of the cellulose hemicellulose that make up two-thirds to three-fourths of plant biomass.

Oscillating catalyst produces stereoblock polymers

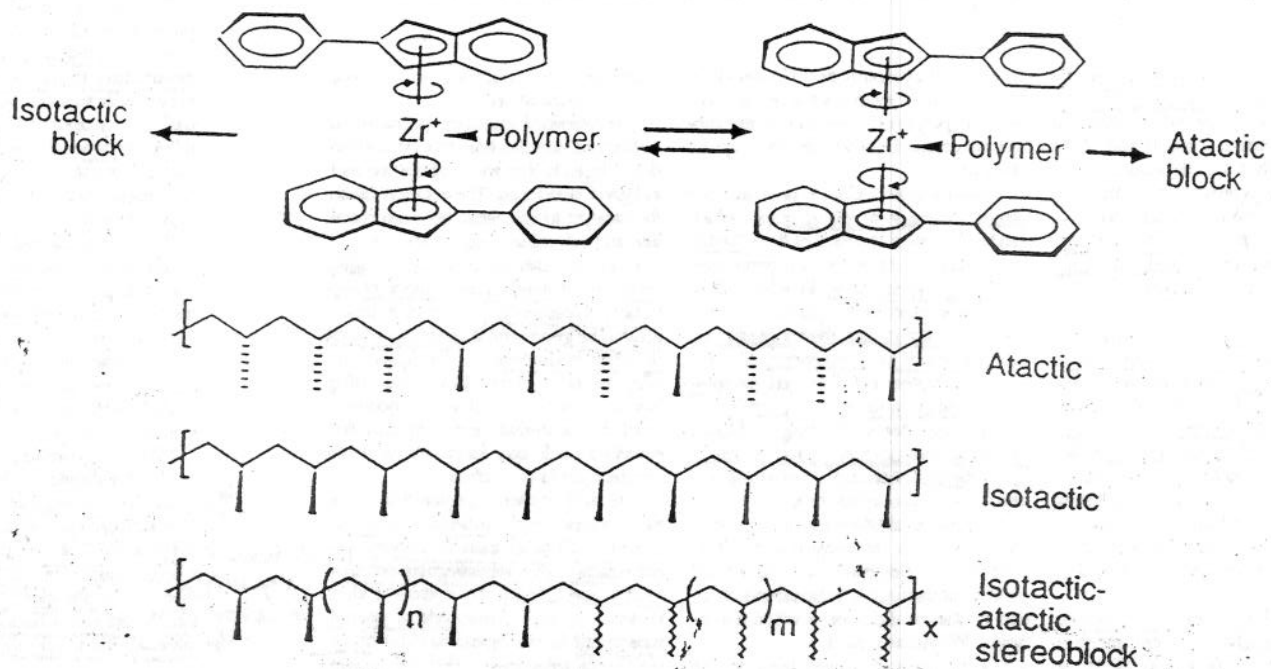


Assignment Due Friday, January 27, 1995

Pick out and list (briefly) five (5) key points in this article.

ELASTOMERIC POLYPROPYLENE

Oscillating catalyst produces stereoblock polymers



C:ENEWS, Jan. 16, 1995

- 1) Uniqueness of system:
 - block copolymers (Atactic and isotactic stereoblocks) achieved not by changing monomer, but by polymerizing the same monomer in a different way.
- 2) Product: Elastomeric polypropylene
 - thermoplastic (recyclable)
- 3) stereochemistry greatly influences PP properties
 - isotactic PP - crystalline thermoplastic
 - Atactic PP - amorphous gum elastomer
 - block copolymer of PP (Atactic + isotactic blocks) - rubbery
- 4) Catalyst system versatile and controllable.
 - can control "isotactic pentad" (5 monomers in sequence) from 6.3% - 28.1
- 5) Interesting and varied PP properties obtainable
 - very elastic material - stretch 8 times L_0 and snap b.
 - crystalline material - stiff and hard.

Transitions in Polymers.

T_g = glass transition temperature

$T > T_g$ rubbery, soft, flexible

$T > T_g + 50$ melt flow

$T < T_g$ rigid, glassy, hard.

Molecular Motions in Polymers.

Activation Energy - (relative)

① molecular vibrations of atoms

$\sim kT$

② Motion of a few atoms (5-6) in the main chain - local motion

$\sim 2-3 kT$

③ Cooperative wriggling and jumping (40-50 carbon atoms). Permits elasticity

$\sim 5-10 kT$

• fast relaxation in reptation theory

④ Long range motion of entire chain to permit Flow.

$\sim 20-50 kT$

• Reptation time scale

* T_g (glass transition) \rightarrow mechanisms 3 & 4 "frozen" out.

Notes: Both Amorphous and Semi-crystalline

polymers CAN have a T_g . Why?

* Answer: semi-crystalline polymer has Amorphous regions.

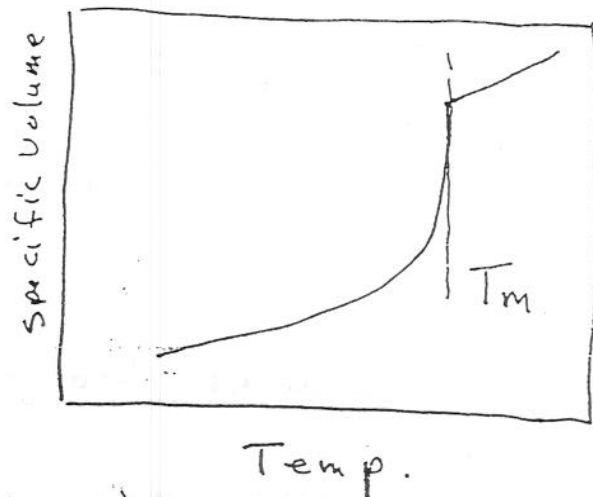
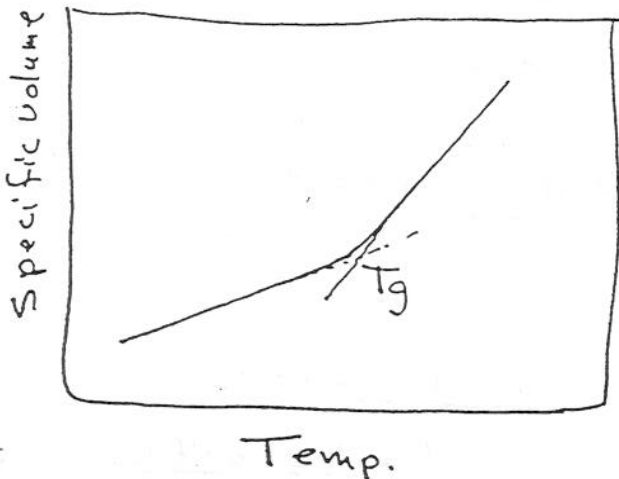
Amorphous

VS

Semi-Crystalline

T_g (no T_m)

T_g and T_m (melting point)



Glass Transition

slope change in v vs. T

v vs T continuous

$\frac{dv}{dT} = \Delta$ discontinuous

2nd order Transition

Melting

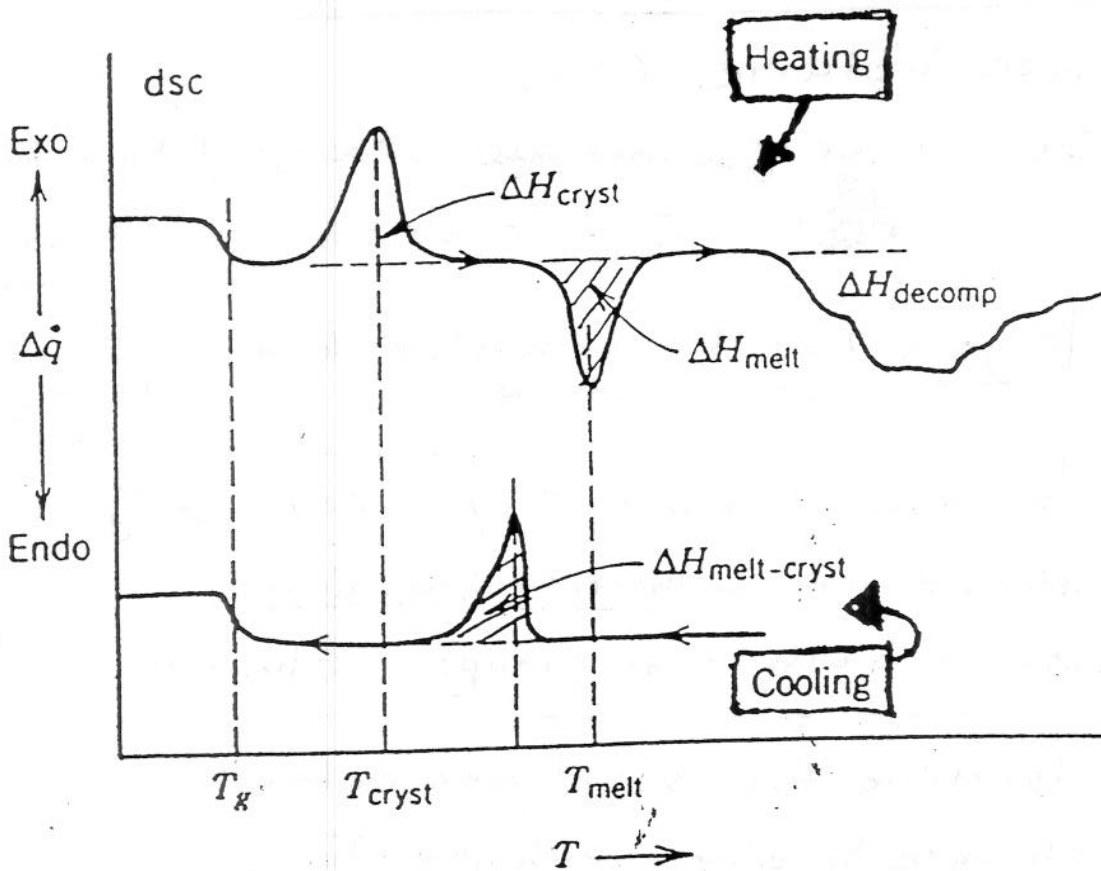
discontinuity in v vs

1st Order Transition

$T_g \Rightarrow$ characterizes the Amorphous phase

$T_m =$ characterizes the crystalline phase

- All polymers have an Amorphous phase (i.e., no polymer is 100% crystalline), therefore all polymers have a T_g .
- Not all polymers have a T_m .
↳ must have crystalline phase to have T_m .



GLASS TRANSITION (T_g): Amorphous regions of polymer

- $\frac{d\Delta H}{dT}$ - second order transition
- endothermic Amplitude change

Crystallization (T_{cryst}): Heating or Cooling - Exothermic

- rate dependent.
- $\Delta H_{cryst} \rightarrow$ % crystallinity

Melting Point (T_m): endothermic (rate dependent)

- $\Delta H_{melt} =$ AREA under melting peak (valley).
- determine % crystallinity of ΔH_{fusion} is known.

$\Delta H_{decomposition}$: endothermic (inert) ; exothermic (AIR)

$\Delta H_{melt-cryst.}$: recrystallization after melting (rate dependent)

Polymers: Amorphous^(T_g only) and semi-crystalline (T_g ; T_m)

- Copolymers : determining transition temperature of each block.
- Blends : compatible \rightarrow single T_g between T_{gA} and T_{gB}
incompatible \rightarrow separate T_{gA} ; T_{gB} .

Factors that Influence T_g .

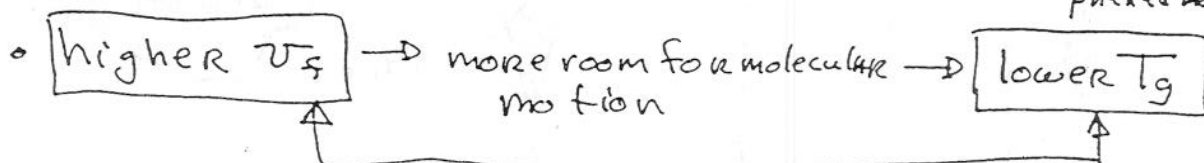
19 (3)

* ① Free Volume (V_f)

V_f = volume of polymer mass not occupied by molecules



$$V_f = V - V_s = \text{specific volume} - \text{volume of solid packed molecules}$$



• universal (?) value: $V_f/V = 0.025 @ T_g$.

Question: How do you increase free volume?

Answer: Bulky side-groups. (however, see #3)

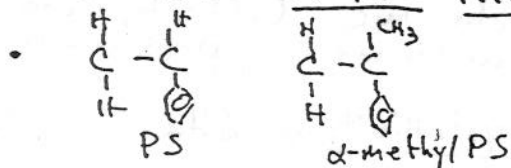
② Attractive forces between molecules.

• stronger bonding \rightarrow higher T_g .

• $\left[\begin{array}{c} \text{H} \\ | \\ \text{C} \\ | \\ \text{H} \end{array} - \begin{array}{c} \text{H} \\ | \\ \text{C} \\ | \\ \text{C} \equiv \text{N} \end{array} \right]_x$ Polyacrylonitrile (strong, polar bonding between chains $\circ\circ$ decomposes before reaching T_g .)

③ Internal mobility of chains (rotational degrees of freedom)

• increased steric hindrance to rotation \rightarrow higher T_g



$$T_{g,PS} < T_{g,\alpha\text{-PS}}$$

④ Backbone stiffness (rigidity) increases T_g .

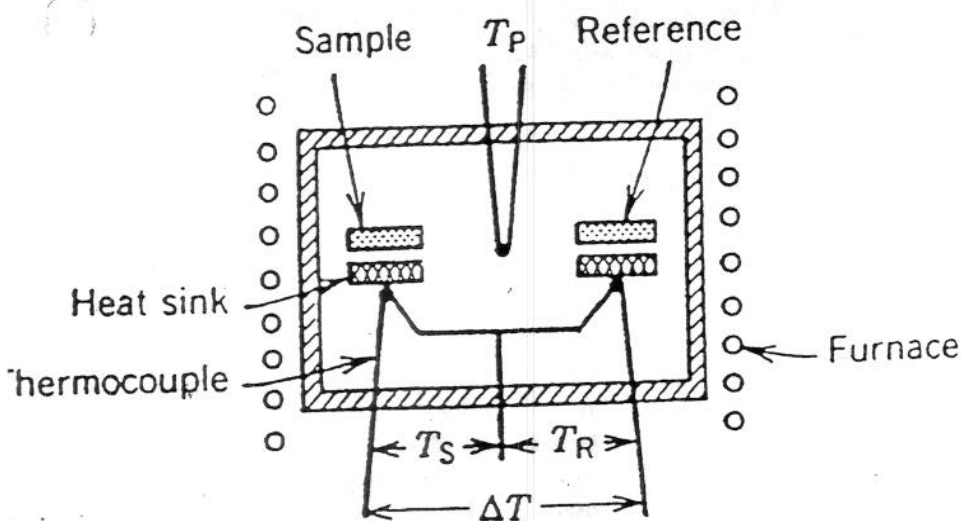
- highly aromatic backbones (LEP's)
- polymers more useful at higher Temps. — difficult to process

⑤ Chain length (molecular weight).

• $T_g = T_g^\infty - \frac{C}{x}$ [$T_g^\infty = T_g$ at infinite M]
 x = chain length.

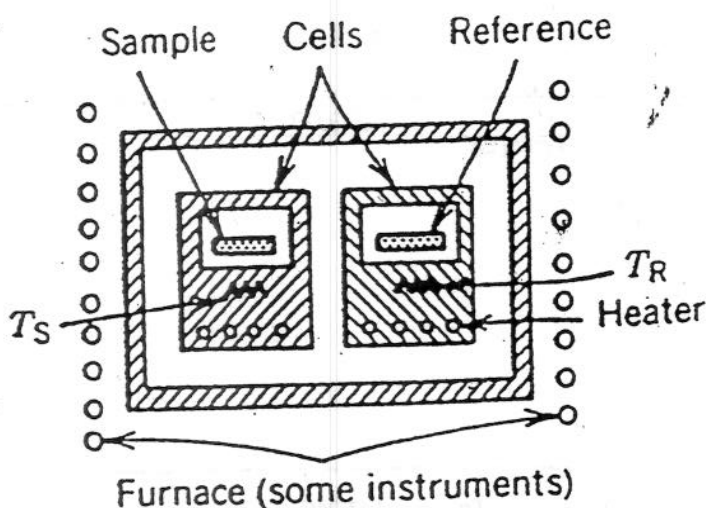
• for most commercial polymers x large $\circ\circ$ $T_g \cong T_g^\infty$

Differential Scanning Calorimetry (DSC)



Instrument Configuration

Technique: Measure difference in HEAT FLOW between a reference pan (T_R) and a sample pan (T_S) [Shimadzu]



Power-Compensated DSC

The two cells are maintained at the same temperature.

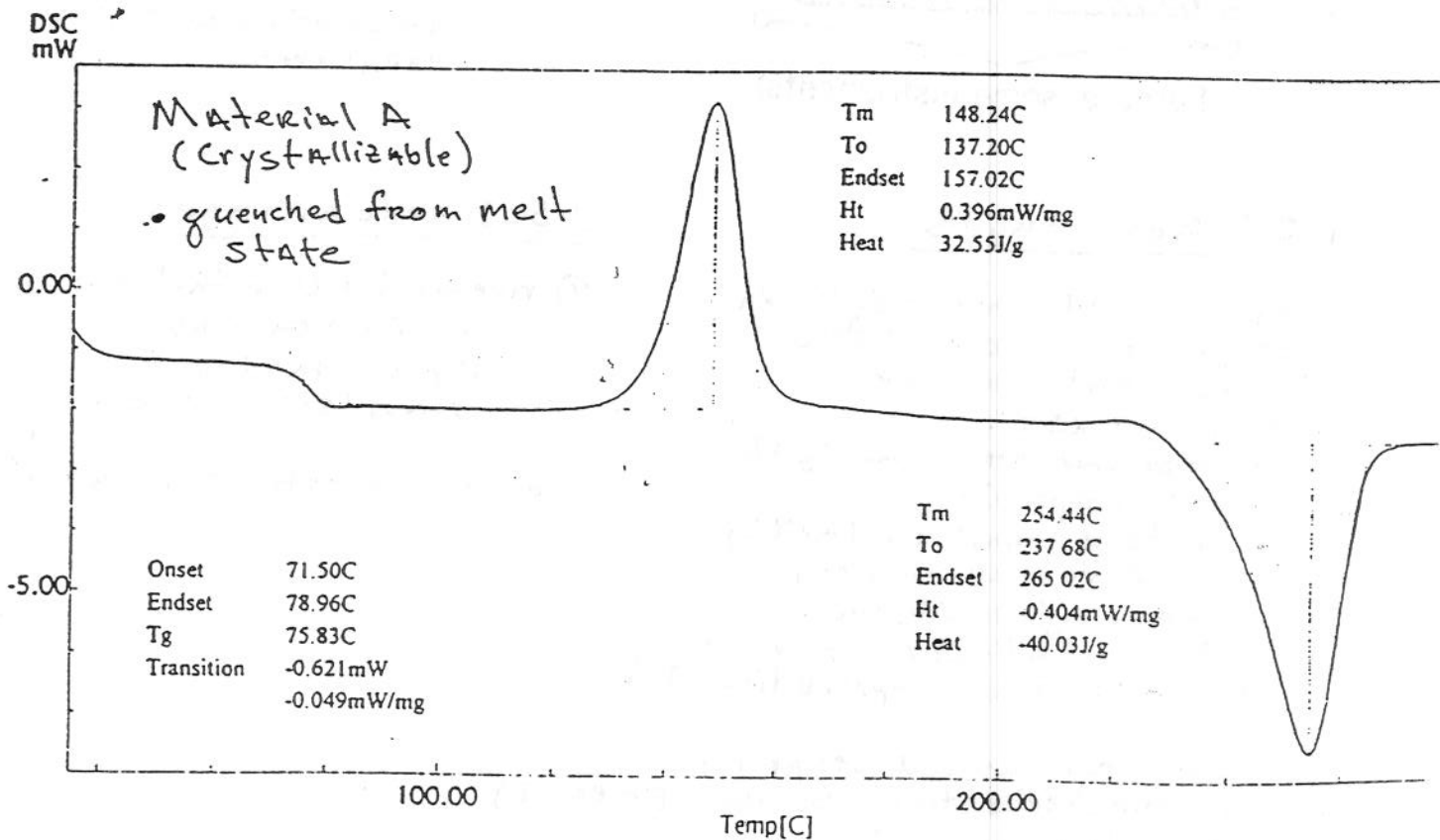
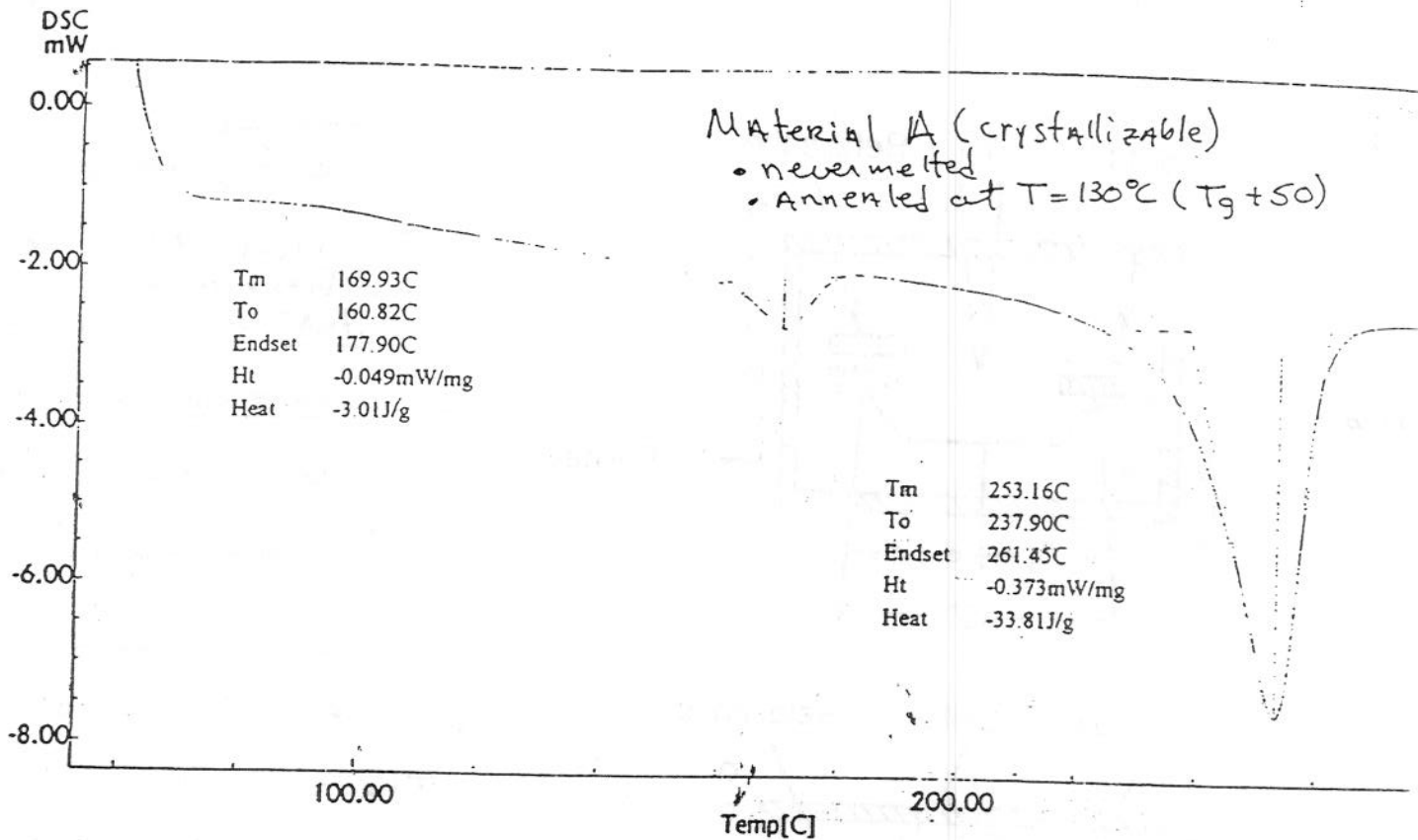
The difference in the power supplied to the reference pan (T_R) and the sample pan (T_S) is measured.

DSC Advantages

- ① speed $0.1^\circ\text{C}/\text{min} - 50^\circ\text{C}/\text{min}$
- ② temp. range $-200^\circ\text{C} - 750^\circ\text{C}$
- ③ ease of calibration.
- ④ Multiple use:
 - temperature transitions (T_g , T_m)
 - heat capacity
 - heats of transition (melting and crystallization)
 - heats of reaction
 - % crystallinity in polymers
 - polymer blend compatibility (T_g)
- ⑤ Industrial use widespread.
 - characterization (routine: Research)
 - quality control

DSC Disadvantages

- ① measures ALL enthalpic events
 - chemical reactions
 - physical transitions
 - stress/strain release
- ∞ data sometimes obscured.



Effect of Copolymerization on T_m & T_g .

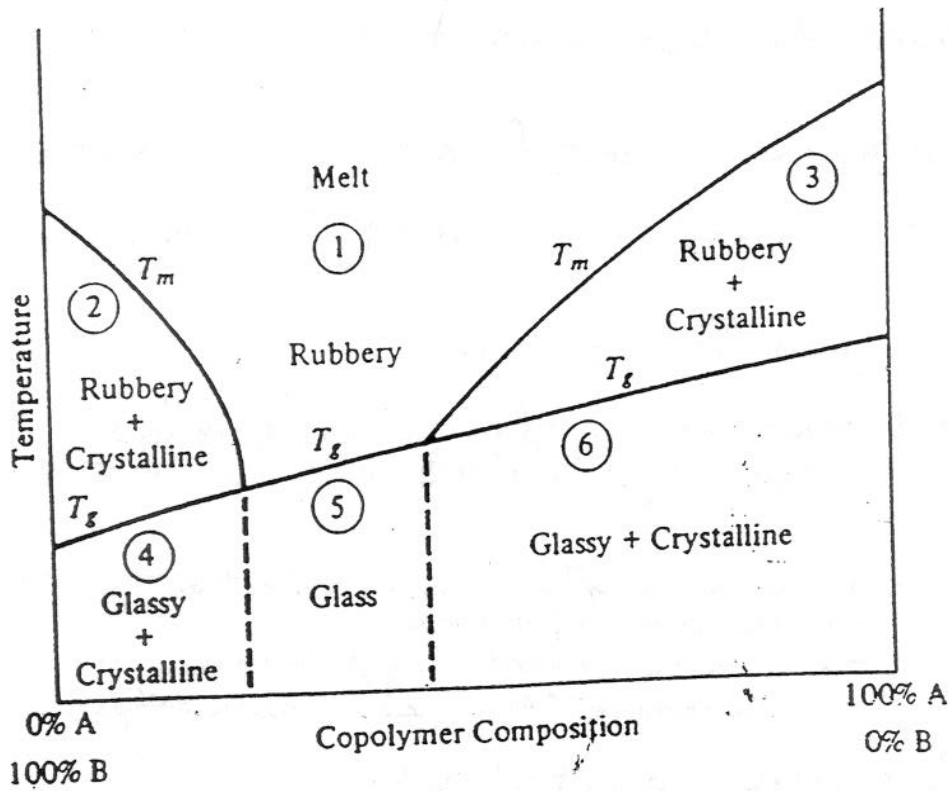
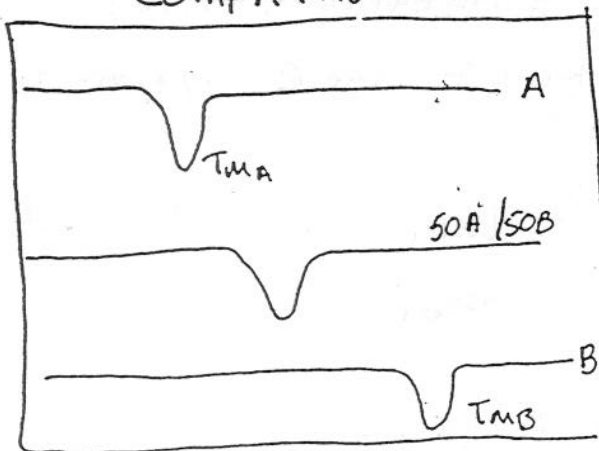


Figure 8.6 Phase diagram for a random copolymer system.

- VARY copolymer composition to control properties.

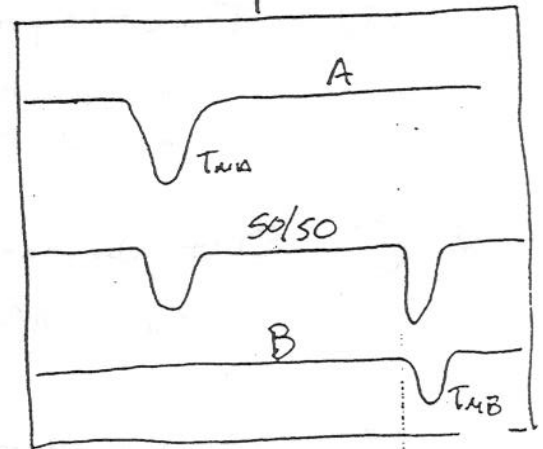
Blends

Compatible



- single phase \rightarrow single T_m

Incompatible



- phase separated $\circ\circ$
each phase has own T_m

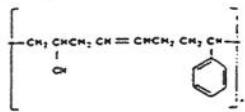
Differential Scanning Calorimetry

Reasons to use this technique:

- ① Polymer identification. (Material I.D.)
 - thermal transitions (T_g, T_m) characteristic of poly.
- ② Polymer Processing.
 - determination of processing "window"
 - typically ($T_g + 50^\circ$) or ($T_m + 10-20^\circ$)
 - determination of processing effect on T_g or T_m
 - residual stresses
 - stress induced crystallization
 - compare "As processed" with 2nd pass through DSC
- ③ Polymer Crystallinity.
 - determination of % Crystallinity in semi-crystalline poly.
 - measure $\Delta H_{\text{crystal}}$ (energy/mass)
- ④ Compatibility of Polymer Blends
 - shift in T_g or T_m with blending.
 - distinct peaks of homopolymers remain → incompatible blend (phase separated)
 - new peaks → compatible blends.
- ⑤ Time-Temperature Crystallization Kinetics
 - growth of crystals with time @ temperature
 - MWD effects.
- * ⑥ Determination of "Filler" Content. (Material I.D.)
 - DSC / Mass Spec. test.
- ⑦ Polymerization Kinetics
 - rate studies for polymer systems.

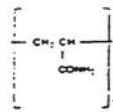
• Melting point temperature range (°C)
 ○ Glass transition temperature range (°C)

The Automode software of the 1020 Series and PC Series Thermal Analysis Systems includes recallable methods for each of the polymers listed in this chart.



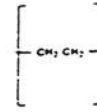
ABS

○ 110° to 125°



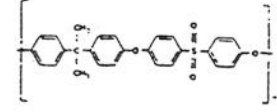
Polyacrylamide

○ 160° to 170°



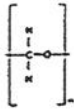
Polyethylene (High Density)

● 130° to 140° ○ -125°



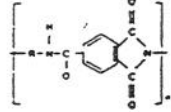
Polysulfone

○ 185° to 195°



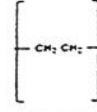
Acetal

● 175° to 185°



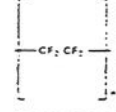
Polyamide-imide

○ 270° to 280°



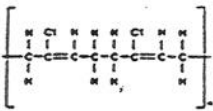
Polyethylene (Low Density)

● 85° to 125° ○ -130°



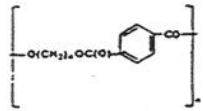
Polytetrafluoroethylene (PTFE)

● 320° to 330° ○ 120° to 130°



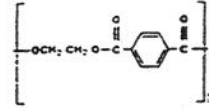
Neoprene

○ -40° to -20°



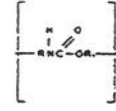
Polybutylene Terephthalate (PBT)

● 220° to 270°



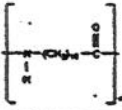
Polyethylene Terephthalate (PET)

● 245° to 265° ○ 70° to 80°



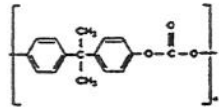
Polyurethane (Thermoplastic)

○ 120° to 160°



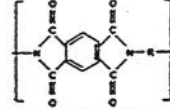
PA11

○ 190° to 200°



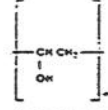
Polycarbonate

○ 140° to 150°



Polyimide

○ 310° to 365°



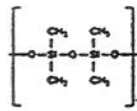
Polyvinyl Alcohol

○ 80° to 90°



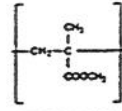
Nylon 12

● 160° to 210°



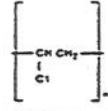
Polydimethylsiloxane (PDMS)

○ -130° to -120°



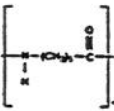
Polymethyl Methacrylate (PMMA)

○ 85° to 105°



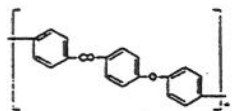
Polyvinyl Chloride (PVC)

○ 65° to 85°



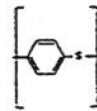
Nylon 6

● 210° to 220° ○ 40° to 60°



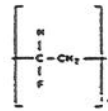
Polyetheretherketone (PEEK)

● 330° to 340°



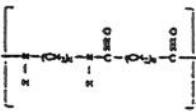
Polyphenylene Sulfide

● 275° to 290° ○ 85° to 95°



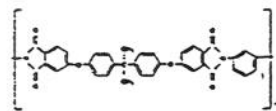
Polyvinyl Fluoride

○ 35° to 45°



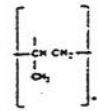
Nylon 6/10

● 215° to 220° ○ 45° to 55°



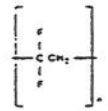
Polyetherimide

○ 215° to 220°



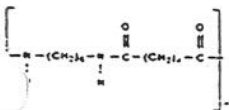
Polypropylene

● 165° to 175° ○ -20° to -5°



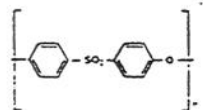
Polyvinylidene Fluoride

● 155° to 185° ○ -30° to -20°



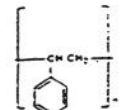
Nylon 6/6

● 240° to 265° ○ 50° to 60°



Polyethersulfone

○ 220° to 230°



Polystyrene

○ 90° to 110°

Order This
 Free Poster Now!
 PE No. PX-TA1B
 Call Your
 Local Office.

1	2	3	4
5	6	7	8
9	10	11	12
13	14	15	16
17	18	19	20
21	22	23	24
25	26	27	28
29	30	31	32
33	34	35	36
37	38	39	40
41	42	43	44
45	46	47	48
49	50	51	52
53	54	55	56
57	58	59	60
61	62	63	64
65	66	67	68
69	70	71	72
73	74	75	76
77	78	79	80
81	82	83	84
85	86	87	88
89	90	91	92
93	94	95	96
97	98	99	100